CO-DIGESTION OF PETROCHEMICAL WASTEWATER WITH ACTIVATED MANURE IN CONTINUOUS STIRRED TANK REACTOR FOR METHANE PRODUCTION

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ABSTRACT

The combined challenges of environmental crisis and declining fossil fuel supplies are driving intensive research focused on alternative energy production. Particularly, today's generation is facing two coexisting problems: the proper management of wastes generated from the industrial sectors, and the scarcity for novel resources of gasoline to meet up energy demand of civilization. Anaerobic co-digestion, a sustainable green technology, presents an outstanding opportunity for both energy conversion and pollution control. Therefore, it has become a core method treating organic wastes on account of its economic benefits of energy generation. The continuous stirred tank reactor (CSTR) can be defined as a sealed-tank digester equipped with mixing facility. Chemical pretreatment coupled with anaerobic co-digestion technology was applied on petrochemical wastewater using CSTR focusing on enhanced hydrolysis and methanogenesis. Batch experiments were performed, with applied H_2O_2 doses of 0.5%, 1% and 1.5% for contact times of 5, 10 and 15 min. Results revealed that 1% H_2O_2 dose (1.0mM Fe^{3+}) for 5 min exposure elevated biodegradability index (BOD/COD) up to 35%. Subsequently, batch experiments were employed with various mixing proportions of petrochemical wastewater (PWW): dairy cattle manure (DCM): beef cattle manure (BCM), such as 25: 37: 38, 40: 30: 30, 50: 25: 25, 60: 20: 20, and 75: 12: 13. Results revealed that PWW: DCM: BCM ratio (50: 25: 25) provided maximum methane production. Although methane production is considered to get introverted by VFA accumulation leading to reactor instability during anaerobic digestion, a 10 mg/L of NH_4HCO_3 dosing and the co-digestion of PWW together with BCM and DCM caused 50% enhancement in methane production, followed by a 98±0.5% reduction in COD at 10 days hydraulic retention time. No VFA buildup was identified. In comparison with the digestion of PWW alone, methane yield increased by 50–60% under mesophilic conditions and 50–65% under thermophilic conditions due to co-digestion. This was induced by an optimum C: N ratio (30:1) of the feed stock ensuring microbial growth and buffering capacity. The anaerobic digestion, biogas generation, and energy assessment were analyzed for ten flow rates; 170, 220, 300, 370, 410, 475, 540, 600, 640 and 680 mL/day. The analytical data revealed that the environmentally complied optimum flow rate was 170 mL/day, for maximum methane generation. As the F/M proportion varied from 0.25 to 2.0 and organic loadings from 6.31-27.14 (g VS/L), however, it has been observed that the methane yield increased from 451.9±15 to 461.5±17 and 519.8±15 to 520.9±16 mL/ g VS as the F/M ratio increased from 0.25 to 0.5 for mesophilic and thermophilic states respectively but decreased gradually even when the F/M ratio increased up to 2. However, considering all the factors F/M ratio of 0.5 was observed to be the optimum to avoid system imbalance. This work may help in minimizing the environmental issues of petrochemical wastewater treatment in the future.

ABSTRAK

Cabaran gabungan krisis alam sekitar dan penurunan bekalan bahan api fosil memacu penyelidikan intensif yang memberi tumpuan kepada pengeluaran tenaga alternatif. Terutama, generasi hari ini menghadapi dua masalah bersama: pengurusan bahan api betul bahan buangan daripada sektor perindustrian, dan kekurangan sumber untuk novel yang baru untuk memenuhi permintaan tenaga yang sesuai. Anaerobik bersama penghadaman, teknologi hijau yang mampan, menyediakan peluang yang luar biasa untuk kedua-dua penukaran tenaga dan kawalan pencemaran. Oleh itu, ia telah menjadi satu kaedah utama untuk mengolah sisa organik disebabkan manfaat ekonomi di dalam sektor tenaga. Reaktor tangki berterusan dikacau (CSTR) boleh ditakrifkan sebagai pencerna dimeteraikan tangki dilengkapi dengan kemudahan pencampuran. Praolehan kimia ditambah pula dengan teknologi anaerobik bersama penghadaman telah digunakan pada petrokimia air sisa menggunakan CSTR memberi tumpuan kepada hidrolisis dipertingkatkan dan methanogenesis. Eksperimen Batch telah dilakukan, dengan gunaan H_2O_2 dos sebanyak 0.5%, 1% dan 1.5% untuk kali kenalan 5, 10 dan 15 min. Hasil kajian menunjukkan bahawa 1% dos H_2O_2 (1.0mm Fe3 +) untuk 5 min pendedahan tinggi indeks biodegredasi (BOD / COD) sehingga 35%. Selepas itu, eksperimen kumpulan bekerja dengan pelbagai perkadaran campuran air sisa petrokimia (PWW): lembu tenusu baja (DCM): lembu daging lembu baja (BCM), seperti 25: 37: 38, 40: 30: 30, 50: 25: 25, 60: 20: 20, dan 75: 12: 13. Hasil kajian menunjukkan bahawa PWW: nisbah BCM: DCM (50: 25: 25) dengan syarat pengeluaran metana maksimum. Walaupun pengeluaran metana dianggap untuk pendiam oleh VFA pengumpulan membawa kepada reaktor ketidakstabilan semasa penghadaman anaerobik, 10 mg / L daripada NH_4HCO_3 dos dan bersama pencernaan PWW bersama-sama dengan BCM dan DCM disebabkan peningkatan 50% dalam pengeluaran metana, diikuti dengan pengurangan 98 ± 0.5% dalam permintaan oksigen kimia di 10 hari masa tahanan hidraulik. Tiada VFA penumpukan telah dikenal pasti. Dalam perbandingan dengan pencernaan PWW sahaja, hasil metana meningkat sebanyak 50-60% di bawah keadaan mesophilic dan 50-65% di bawah keadaan thermophilic kerana bersama penghadaman. Ini telah didorong oleh C optimum: nisbah N (30: 1) stok suapan memastikan pertumbuhan mikrob dan kapasiti buffering. Pencernaan anaerobik, penjanaan biogas, tenaga dan penilaian dianalisis bagi sepuluh kadar aliran; 170, 220, 300, 370, 410, 475, 540, 600, 640 dan 680 mL / hari. Data analisis menunjukkan bahawa kadar aliran optimum yang dipatuhi alam adalah 170 mL / hari, untuk generasi metana maksimum. Sebagai nisbah F / M diubah 0.25-2.0 dan beban organik 6.31-27.14 (g VS / L), walau bagaimanapun, ia telah diperhatikan bahawa hasil metana meningkat daripada 451.9 ± 15-461.5 ± 17 dan 519.8 ± 15-520.9 ± 16 mL / g VS sebagai nisbah F / M meningkat 0.25-0.5 untuk negeri mesophilic dan thermophilic masing-masing tetapi menurun secara beransur-ansur walaupun nisbah / M F meningkat sehingga 2. Walau bagaimanapun, memandangkan kesemua faktor nisbah F / M 0.5 diperhatikan untuk menjadi yang optimum untuk mengelakkan ketidakseimbangan sistem. Kerja ini boleh membantu dalam mengurangkan isu-isu alam sekitar rawatan air sisa petrokimia pada masa akan datang.

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A	Cross-sectional area
ACD	Anaerobic co-digestion
AD	Anaerobic digestion
AFBR	Anaerobic fluidized bed reactor
AHMPR	Anaerobic hydrogen and methane production reactor
AM	Activated Manure
ASB	Activated sludge biomass
ASBR	Anaerobic sequencing batch reactor
ASCD	Anaerobic semi continuous digester
ATCC	American type culture collection
BCM	Beef cattle manure
BOD	Biochemical oxygen demand
BOD_5/COD	Bio-degradability index
BDOC	Biodegradable dissolved organic carbon
CA	Catalase activity
CBCTT	Chemical and biological coupled treatment technology
C/N	Carbon to nitrogen ratio
COD	Chemical oxygen demand
COD_f	Feed Chemical oxygen demand
COD_{in}	Influent chemical oxygen demand

CSTR	Continuous stirrer tank reactor
DCM	Dairy cattle manure
DOC	Dissolved organic carbon
F/M	Food to micro-organism ratio
FAFBR	Flocculant-anaerobic fluidized bed bioreactor
FSAD	Full scale anaerobic digester
HRT	Hydraulic retention time
H_2O_2	Hydrogen peroxide
IBR	Integrative biological reactor
MSW	Municipal solid waste
OLR	Organic loading rate
OHP	Oxidation by hydrogen peroxide
PWW	Petrochemical wastewater
Q	Flow rate
SD	Standard deviation
SRT	Sludge retention time
SS	Suspended solids
TKN	Total Kjeldahl nitrogen
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorous
TSS	Total suspended solids
TT	Thousand tons

UASB	Upflow anaerobic sludge blanket
UASSR	Up-flow anaerobic solid state reactor
UNFT	Unfiltered Turbidity
VFA	Volatile fatty acid
VSS	Volatile suspended solids
° C	Degree Celsius
KM	Kilometer
min	Minute
cm	Centimeter
cm^2	Square centimeter
d	Diameter
g	Gram
H	Height
h	Hour
Kg	Kilogram
L	Liter
M	Micro mole
m^3	Cubic meter
V	Velocity
µ	Micro (10^{-6})
P	Phosphorous
N	Normality

TS	Total solids
NH_4HCO_3	Ammonium bicarbonate
MFBR	Mesh filter bioreactor
SAMR	Submerged anaerobic membrane reactor
SMAR	Self-mixing anaerobic reactor
SCR	Semi continuous reactor
STP	Standard temperature and pressure

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Currently, the world is confronting two parallel issues: i) the appropriate control of waste originating from manufacturing areas and ii) the lack of innovative fuel resources to meet increasing energy requirements (Harsono et al., 2014; Tommasi et al., 2013). Simultaneous ecological battles and deteriorating fuel supplies have inspired laborious studies to improve energy reserves. The most common substitute reserve stock for fossil fuels in the petrochemical subdivision is biomass (Bustamante et al., 2013; Serrano et al., 2013). Nevertheless, surplus waste harvests can also act as distinct fossil fuel reserve stocks. Particularly, at the start of the 21st century, the world is facing environmental contingency of wastewater management and global warming due to population rise, industrialization, solid waste generation, urbanization and unplanned waste management. Integrating these into whole generates huge untreated industrial and domestic wastewater which is carcinogenic to the human beings. In particular, wastewater generated from petrochemical industries is a complex mixture of polycyclic aliphatic and aromatic petroleum hydrocarbons (Bierkens and Geerts, 2014; Ghorbanian et al., 2014; Métayer et al., 2014; Yanto and Tachibana, 2014) in which aromatic portion cannot be easily digested by commonly practiced methods. Petrochemical wastewater

(PWW) possesses much oxygen undermining potential (COD 1-60 g/L) as industrial wastewater becomes huge challenge to meet progressively strict environmental guidelines (Lakatos et al., 2014; Maretto et al., 2014; Patel and Madamwar, 2002; Shavisi et al., 2014; Wang et al., 2014a). The deficiency of wastewater management absolutely affects natural divergence of the aquatic ecosystems, disordering the elementary integrity of total ecosystems. So, the prevention of continuous pollution caused by petrochemical effluents is obligatory. Anaerobic digestion (AD) presents an outstanding opening for energy conversion and pollution minimization mutually (Alvarez et al., 2014; Sankaran et al., 2014; Zhang et al., 2014a).

The conventional treatments include gravitational separation, centrifugation, ozonation, wet oxidation, application of coagulants, flocculants, flotation, ultra filtration or sorption and advanced treatment process (Parilti, 2010; Vallejo et al., 2015; Zhuang at al., 2014). The anaerobic digestion system among all treatment options had been accepted as the fundamental one of a progressive mechanism for environmental safeguard (Siddique et al., 2014). To meet up growing requirement for energy and financially-advantageous treatment strategy, AD system has become the motivation of universal consideration (Hidalgo and Marroquín, 2014). In comparison with former technologies, the main benefits of AD system are minor sludge yield, minimum budget, great energy feedback and process stability. Besides, it provides an optimistic environmental influence accommodating waste management with net energy generation. The technology also permits the utilization of effluent as compost. Numerous researchers have studied anaerobic digestion since the last decade (Dareioti and Kornaros, 2014; Kythreotou et al., 2014; Montañés et al., 2014; Ortner et al., 2014; Theofanous et al., 2014; Vrieze et al., 2014; Wang et al., 2014b; Yu et al., 2014; Zhang et al., 2014b). Nevertheless, despite these benefits, anaerobic digestion is not practiced widely in PWW treatment due to its slow reactions, leading to long hydraulic retention time (HRT), volatile fatty acid (VFA) accumulation, and poor process stability. Hence; this study on this basis is focused.

Anaerobic digestion is accomplished via three basic mechanisms; namely hydrolysis, acidogenesis and methanogenesis (Niu et al., 2014 and Lu et al., 2013). Notable that hydrolysis is considered to be a rate-defining stage in AD; specifically, due to recalcitrant substrates. Fatty acids in wastewater have an inhibitory impact on many microorganisms, which makes biological degradation difficult (Chandra and Mohan, 2014 and Niu et al., 2013). Pretreatment might play a role in improving biochemical degradation efficiency (Wang et al., 2014c; Yu et al., 2014). Many pretreatments aspire to solubilize or hydrolyze the compounds to improve degradability in biotic reactors. Those consist of physical dimension reduction, thermal hydrolysis, ultrasonic treatment, chemical treatment by acid or alkali, ozonation and oxidation by H_2O_2. H_2O_2 is a versatile, vigorous oxidative agent that reacts via a hydroxyl radical mechanism with an oxidizing potential of 2.6V, which reduces chemical oxygen demand (COD), produces H_2O and CO_2, and enhances biodegradability of organic matters.

Even if there were widespread application of AD, the methane generation would be squat and related to elevated nitrogen and lignocellulose content (Rajagopal et al., 2013; Yenigün and Demirel, 2013). Hence, co-digestion of pretreated PWW with beef cattle manure and dairy cattle manure could offer an efficient solution, with marked reduction in volatile fatty acid (VFA) accumulation and improved reactor stability. In this study, we focused on the consequence of various mixing proportions on methane generation latent and stability of continuous stirred tank reactor under different conditions.

A CSTR can be defined as a closed-tank digester equipped with mixing facility (Diana et al., 2013; Yang et al., 2013). Mechanical instigator renders much area of contact between substrate and microorganisms thus ameliorating gas production. Over and above feeding of anaerobic digesters are amalgamated to assure competent transmission of organic compound for the active bacteriological biomass, to discharge gas bubbles grabbed in the system and to avoid precipitation of heavier coarse substance (Zhang et al., 2014c; Ward et al., 2008).

1.2 CHEMICAL PRETREATMENT AND ANAEROBIC CO-DIGESTION IN CONTINUOUS STIRRED TANK REACTOR

The application of H_2O_2 as an oxidizing auto catalyst already proved treating halogenated hydrocarbon endures in waste water treatment (Oh et al., 2014; Zhang and Li, 2014). To degrade variety of hazardous wastes in situ chemical oxidation (ISCO) has been used as an encouraging inventive technique (ITRC, 2001; ITRC, 2005). H_2O_2 oxidation mechanism might be made of a struck via OH radicals on the carbon-hydrogen chain of fatty acids. OH^- radicals possess muscular capability to breakdown the aromatic ring fixed to hydroxyl groups exists in fatty acids. These accelerate development of water-soluble complexes through cogitation of hydrogen and addition of oxygen atoms through contribution of ferrous or ferric ions. This process generates minor aliphatic compounds, resulting from infringement of lengthier hydrocarbon chains of fatty acids and lastly provokes mineralization of preliminary organic matters. In combination of biological treatment, make oxidation by hydrogen peroxide (OHP) an innovative alternative for advanced waste water treatment (Apollo et al., 2014).

Habitually, in industrial effluents, fraction of digestible COD which may be symbolized by biodegradable dissolved organic carbon (BDOC) is relatively low (Apollo et al., 2014; Tripathi et al., 2011). Hence, to enhance the treatment productivity, an evocative oxidant that enhances BDOC of raw wastewater is obligatory. H_2O_2 can transubstantiate several refractory organic compounds to biodegradable ones, i.e., BDOC that can be eliminated simply via biodegradation. Earlier researchers reported that H_2O_2 might enhance biodegradability of organic waste products producing most effective intermediates like OH^- radicals in presence of Fe^{2+} (Babu et al., 2010; Long et al., 2007; Socías et al., 2013). Scientists reported that OH radicals produced via Fenton-like mechanism are proficient of oxidation of plentiful organic matters, including diesel (Ferguson, 2004; Kong et al., 1998; Li et al., 2013; Prabir et al., 2011; Yeh et al., 2008;), chlorinated ethylenes (Yeh et al., 2003), aromatic hydrocarbons (Ahad et al., 2008; Yeh et al., 2008), 2,4-dichlorophenol (Wang et al., 2013 and Zhou et al., 2008), and 4-chlorophenol (Kozmér et al., 2014 and Zhou et al., 2008).

Catalase, an antioxidant can break down H_2O_2 into water and oxygen (Milton, 2008). To split H_2O_2 into molecular O_2 and H_2O, catalases use a two-electron transfer mechanism (Guwy et al., 1999). One unit of catalase activity corresponds to disintegration of 1 µmole of H_2O_2 per minute at standardized conditions, providing a gas flow of 11.2 µl of O_2/min at Standard temperature and pressure (STP) (Guwy et al., 1999). To neutralize H_2O_2 toxicity effect on activated microbial biomass catalase activity has been employed before anaerobic co-digestion.

Methane yield of AD system might be enriched by Co-digesting sewage sludge together with agro agricultural wastes or municipal solid waste (MSW) (Alatriste- Ferrer et al., 2014; Mondragon et al., 2006; Romano and Zhang, 2008; Solli et al., 2014; Xing et al., 2014; Zheng et al., 2014). Moreover, co-digestion of cattle manure and MSW (Borowski et al., 2014; Hartmann and Ahring, 2005; Lindmark et al., 2014) provided increased methane yield. A predominantly resilient cause for co-digestion of wastes is the appropriate fixation of carbon-to-nitrogen (C: N) ratio. The optimal C: N ratio of 25–30:1 is usually utilized by microorganisms. Nonetheless C: N ratios may frequently be significantly lesser than this, for instance the C: N ratio of sewage sludge is around 9:1 (Kizilkaya and Bayrakli, 2005). Wastewaters can differ extensively in C: N values. The two-stage reactor through biomass retention has been investigated to reflect the proficiency of dependable performance having C: N ratios less than 20 (Mata-Alvarez, 2002). The ideal C: N ratio may be achieved by co-digesting low and high C: N ratio wastewater like as biomass. In order to increase methane production compared to the conventional method co-digestion has been chosen in this study.

Temperature plays a significant role as an operational parameter for AD method (Siddique et al., 2014). The effect of temperature on bacterial growth and degradation frequency may be demonstrated by the Arrhenius equation (Batstone et al., 2002; Hao et al., 2002; Siegrist et al., 2002). AD at thermophilic conditions presents numerous benefits like enhanced reaction frequency and ameliorated bio-digestibility of organics (Kim et al., 2002; Rintala, 1997; Yu et al., 2014). Noticeable that an alteration from mesophilic to thermophilic conditions is conducted by a remarkable (over 80%) and prolonged (over 4 days) reduction in methane yield because of acclimatization of methanogens to thermophilic state (Van Lier et al., 1992; Visser et al., 1993). Nonetheless, mesophilic methanogens were exposed to bear short-range temperature rise (Speece and Kem, 1970 and Ahn and Forster, 2002) or sludge interchange between mesophilic and thermophilic digesters (Song et al., 2004). Therefore, both conditions were executed to study the performance of CSTR.

This study also proposes the application of ammonium bicarbonate (NH_4HCO_3), due to its buffering capability opposite to acidity throughout operational period and also to maintain bacteriological population balance. Therefore, significant roles will be performed by NH_4^+ as the recommended microbial nutrient for nitrogen and buffering capability in an anaerobic reactor (Gerardi, 2003). Nonetheless, excessive NH_4HCO_3 concentrations create free ammonia toxicity particularly for methanogensis (Niu et al., 2013; Sawayama et al., 2004). Hence, the optimal dosage for NH_4HCO_3 applied as supplementation in AD system should be investigated.

The co-digestion of petrochemical wastewater with activated manure has not been widely examined; the abrupt pH drops resulting in reactor failure and volatile fatty acid (VFA) accretion have not been studied, nor have the optimal ratios for CH_4 production. Furthermore, no previous studies on the simultaneous investigation of ecological, energetic and financial features have been published. Consequently, the work presented here may help lessen the environmental issues related to petrochemical manufacturing. This research focuses on the environmental, energy-related, and fiscal potential of anaerobic co-digestion (ACD) of PWW with AM in a CSTR operated in thermophilic conditions. Laboratory-scale trials examining COD elimination ability, the rank of treated samples and the optimal CH_4 yield under distinct waste blends (100 % PWW; 90 % PWW/10 % AM; 80 % PWW/20 % AM; 70 % PWW/30 % AM; 60 % PWW/40 % AM; 50 % PWW/50 % AM; 40 % PWW/60 % AM; 30 % PWW/70 % AM; 20 % PWW/80 % AM; 10 % PWW/90 % AM; 100 % AM) are explained throughout the text.

Although anaerobic bio-digestion is being extensively applied to the industrial treatment plants, the optimum flow rate to feed the bio-digester still remains as the burning question. Consequently, our research motivation was to Figure out the optimum flow rate that optimized both biogas generation and bio-digestion. Incoming wastewater must flow through a treatment plant at a rate that allows microorganisms sufficient time to consume the incoming food and to settle properly. High flows can shorten the time necessary for the full treatment of wastewater. Extremely high flows can wash microorganisms out of the plant through the final clarifier. There is an obvious influence of influent flow rate on the biogas generation during anaerobic process. It shows a vast research gap in determining the optimal flow rate during the industrial application of the bioreactors. Moreover, being confused about the optimal flow rate during reactor operation represents a huge energy loss taking place every year in the industrial sector. A definite flow rate has become increasingly important to comply with the increasingly stringent environmental regulations by providing adequate treatment of effluents from industrial sources. Therefore, to determine the influence of feed flow rate on the biogas generation and the degradation of wastewaters from the petroleum refinery at Terengganu, Malaysia using a continuous CSTR-type bio-digester was one of the key objectives of this present study.

Incoming wastewater to a treatment plant provides the food that microorganisms need for their growth and reproduction. This food is mostly organic material. The more soluble the organic material is, the more easily microorganisms can use it. Therefore, the optimum food to microbe ratio to operate the CSTR still remains unknown. In particular, the influence of the F/M proportion on the anaerobic co-digestion of PWW and activated manure operating under both mesophilic and thermophilic conditions has not been studied extensively. Consequently, our research motivation was to investigate the effect of F/M proportion, which optimized both biogas generation and bio-digestion. Therefore, the principal objective of this work was to observe the influence of F/M proportions (0.25 to 2.0) on biogas generation and organic pollutants reduction from PWW under mesophilic and thermophilic states.

1.3 PROBLEM STATEMENT

Anaerobic digestion is being used effectively in numerous fields such as petrochemical industries, POME industries, distillery industries, olive-oil industries, piggery wastewater, dairy wastewater, fishery wastewater, municipal wastewater, and slaughterhouse wastewater to protect environmental pollution as well as to generate energy (Latif et al., 2011). Particularly for petrochemical wastewater, investigations reported that aldehydes, acids, alcohols, and esters might be employed for methane yield after lengthy acclimatization (Siddique et al., 2014). The existence of hydroxyl groups and a growing carbon chain decreased the toxicity of complexes to the digester microflora. Adaptations to aromatic ring and double-bond compounds are time consuming. The most common design applied in AD is continuous stirred tank reactor. The major problem of the reactor is prolonged retention time and minor gas yield. Presently, anaerobic digestion is facing following impairments:

[1] sluggish reactions, that need lengthier HRT and indigent system stability in commonly practiced designs

[2] operational failure is caused by an abrupt drop of pH & accumulative concentration of VFA

[3] insufficient buffering control & distraction of bacterial population stability between non-methanogen & methanogen to transform carbonaceous organic to CH_4

[4] sludge sustaining problem with multi-chamber fixed film anaerobic treatment remained unsolved

[5] sludge washed out from the anaerobic up-flow fixed-film reactor

[6] lower COD removal by anaerobic hybrid reactor therefore, pollution control with energy production strategy of anaerobic digestion process still facing stability challenge and retention time challenge.

1.4 OBJECTIVES OF RESEARCH

This research focuses on the anaerobic co-digestion of petrochemical wastewater with beef and dairy cattle manure in CSTR having chemical pretreatment strategy. Anaerobic co-digestion is proposed based on the biodegradation technique to avoid slow reaction, prolonged startup, volatile fatty acid accumulation, reactor failure, sludge washout and to enhance methane production capability of CSTR. This research framework combines chemical and biological treatment system much effectively. It can be applied in petrochemical industries, POME industries, distillery industries, olive-oil industries, slaughterhouse wastewater etc. Therefore, it meets up the energy demand cost effectively.

The objectives of this research are projected below:

i. To characterize petrochemical wastewater and determine the optimal H_2O_2 pretreatment dosing before anaerobic co-digestion of petrochemical wastewater and cattle manure in continuous stirred tank reactor for COD reduction and enhanced biodegradability
ii. To determine the optimal mixing proportion of Petrochemical wastewater and cattle manure during anaerobic co-digestion in continuous stirred tank reactor for COD reduction and enhanced bio-methane production
iii. To determine the optimal flow rate during anaerobic co-digestion of Petrochemical wastewater and cattle manure in continuous stirred tank reactor for COD reduction and enhanced bio-methane production
iv. To determine the optimal food to microbe ratio (F/M) during anaerobic co-digestion of Petrochemical wastewater and cattle manure in continuous stirred tank reactor for COD reduction and enhanced bio-methane production
v. To determine the optimal ammonium bicarbonate dosing and to reduce the VFA accumulation during anaerobic co-digestion of petrochemical wastewater and cattle manure using continuous stirred tank reactor for system stability

CHAPTER 1

INTRODUCTION

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CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

This section explains the research framework. Materials, experimental set up, inoculum, analytical methods have been demonstrated clearly. The details of experimental outcome have been discussed further in the relevant chapters.

3.2 RESEARCH FRAMEWORK

In the proposed system, combination of chemical and biological treatment technology focusing on hydrolysis and methanogenesis was tried. With a view to achieve the research objectives, H_2O_2 were selected as pretreatment tool and continuous stirred tank reactor (CSTR) was employed as the biological treatment tool. However, in each case batch treatment was performed strictly. On the basis of batch treatment results, reactor operation was carried out. Batch treatment was performed with trial and error methods. Statistical analysis was also worked out with a view to check the validity of the results. Figure 3.1 elaborates the research framework to provide a crystal clear view on the experimental strategy.

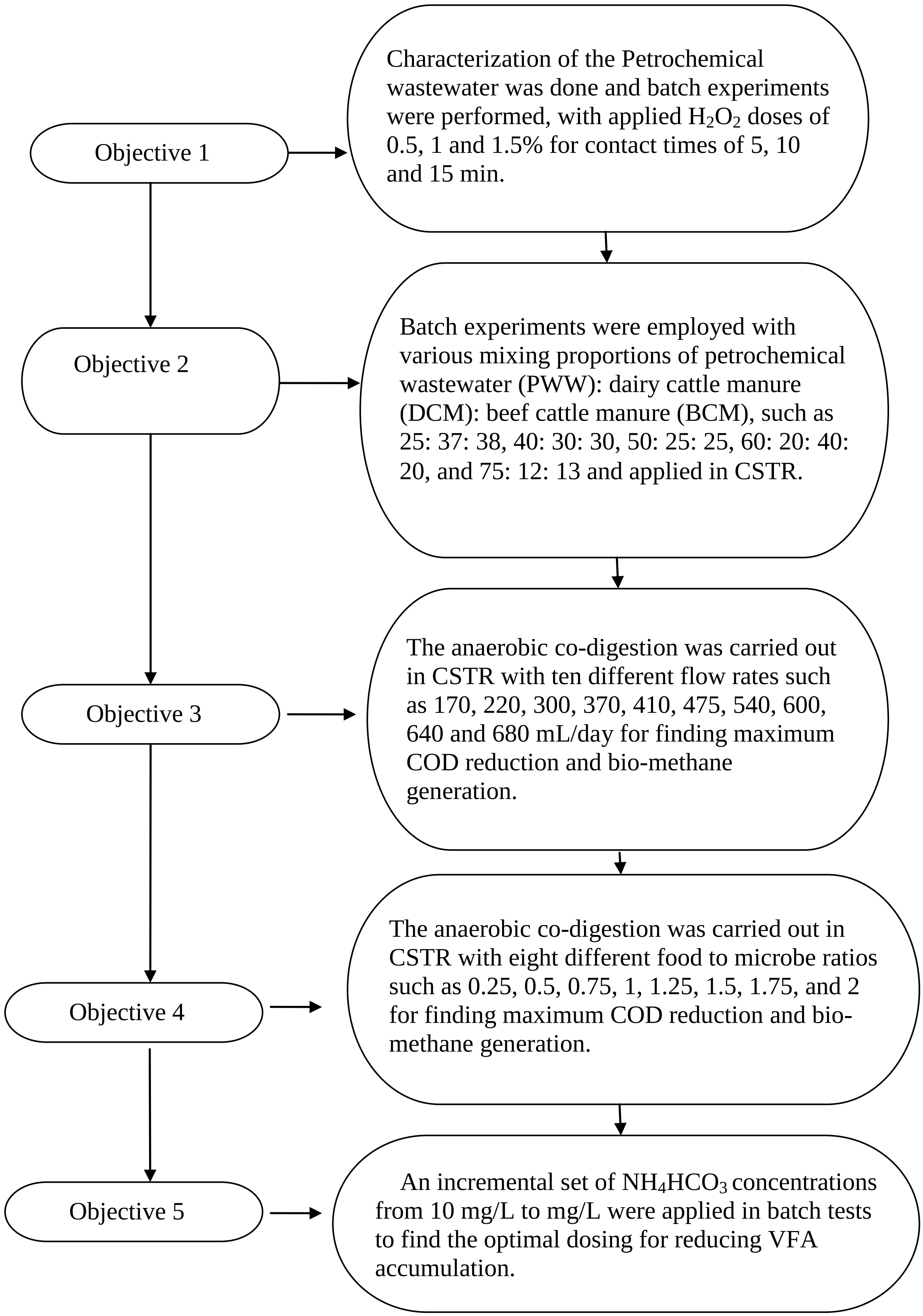

Figure 3.1: Structure of experimental plan

3.3 SAMPLE COLLECTION

A 100-L sample of petrochemical waste water (PWW) was accumulated in containers from discharge receiving stream of the Petronas Penapisan (Terengganu) Sdn Bhd (petroleum refinery) at Terengganu, Malaysia. However, hydrocarbon degrading bacterial strain *pseudomonas aeruginosa* ATCC 27853 was purchased from BioSynTech Malaysia Group Sdn Bhd as it provides the maximum degradation efficiency. The main petrochemical product of this refinery is naphtha. The capacity of this refinery has been reported as 2.4 million (metric ton per annum) mtpa. However, naphtha, usually denotes to numerous combustible liquid mixes of hydrocarbon, that is a constituent of natural gas condensate or a refinement outcome from petroleum, coal tar or peat boiling in a definite limit and comprising specific hydrocarbons. It's an extensive covering among the lightest and most volatile portions of the liquid hydrocarbons in petroleum (Rune et al., 2004). Naphtha is a colorless to reddish-brown volatile aromatic liquid, very similar to gasoline (Rune et al., 2004). As observed the company at this moment is adopting chemical treatment which can only capable to remove COD. But the treatment technology is not that effective to provide any energy as feedback. Even though, there exists a potentiality to produce significant amount of energy using anaerobic digestion process.

3.4 SAMPLE PRESERVATION

Approximately 100 kg partially digested beef cattle manure (BCM) and dairy cattle manure (DCM) was collected duly from ejection of average-sized farm in Gambang, Malaysia. The PWW, BCM and DCM were placed in compact frost containers and transferred to preservation cold room. The temperature was maintained at 4°C during preservation. Effluent pH was maintained around 6.5 by addition of 6N NaOH solution. Alkalinity was maintained around 1500–1700 mg/L $CaCO_3$ with